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(54) Carbon fibre-thermoplastic
resin composite

ing the mixture.

(57) A carbon fibre-thermoplastic resin composite comprises (a) highly crystalline carbon fibres having undergone no surface treatment, possessing a crystallite size of 50 Å or over in the direction of the [001] plane and possessing a regular crystal surface, and (b) a highly crystalline thermoplastic resin allowed to attain epitaxial nucleation radially on the peripheral surface of said carbon fibres and subsequent overgrowth crystallisation in the cylindrical form, whereby the carbon fibres and the thermoplastic resin are bound at their interface by virtue of van der Waals force. The invention also includes a method for the manufacture of the composite by incorporating the carbon fibres in the molten resin and cool-

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Fig.1

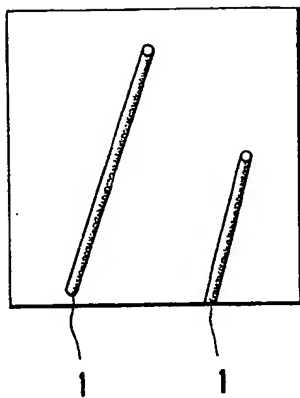


Fig.2

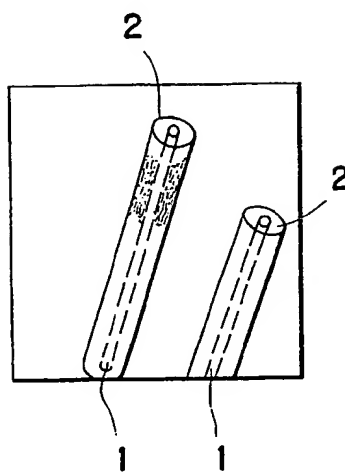


Fig.3

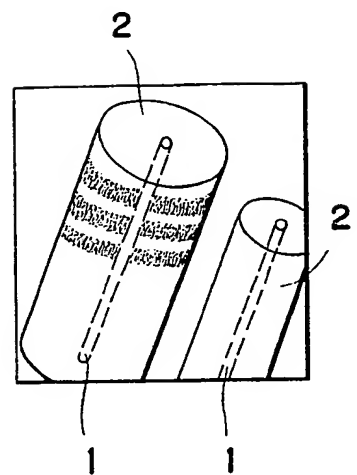


Fig.4

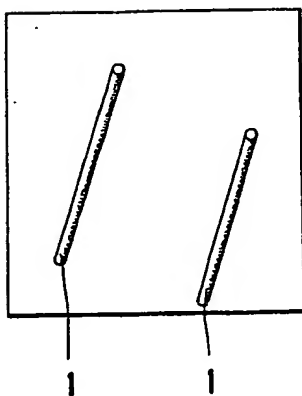


Fig.5

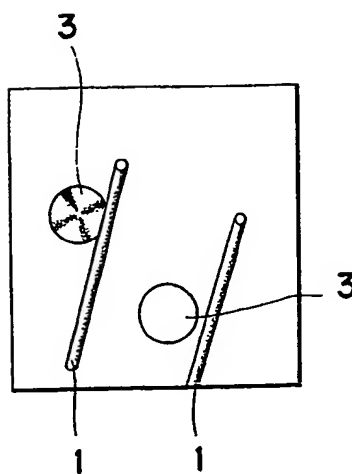


Fig.6

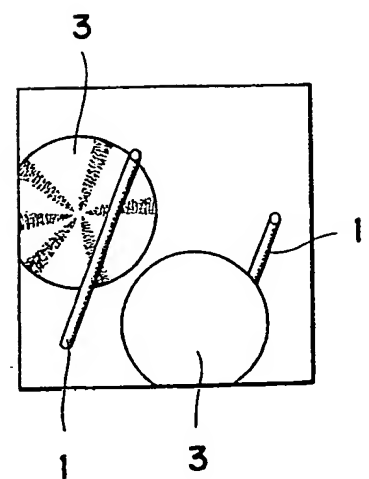


Fig. 7

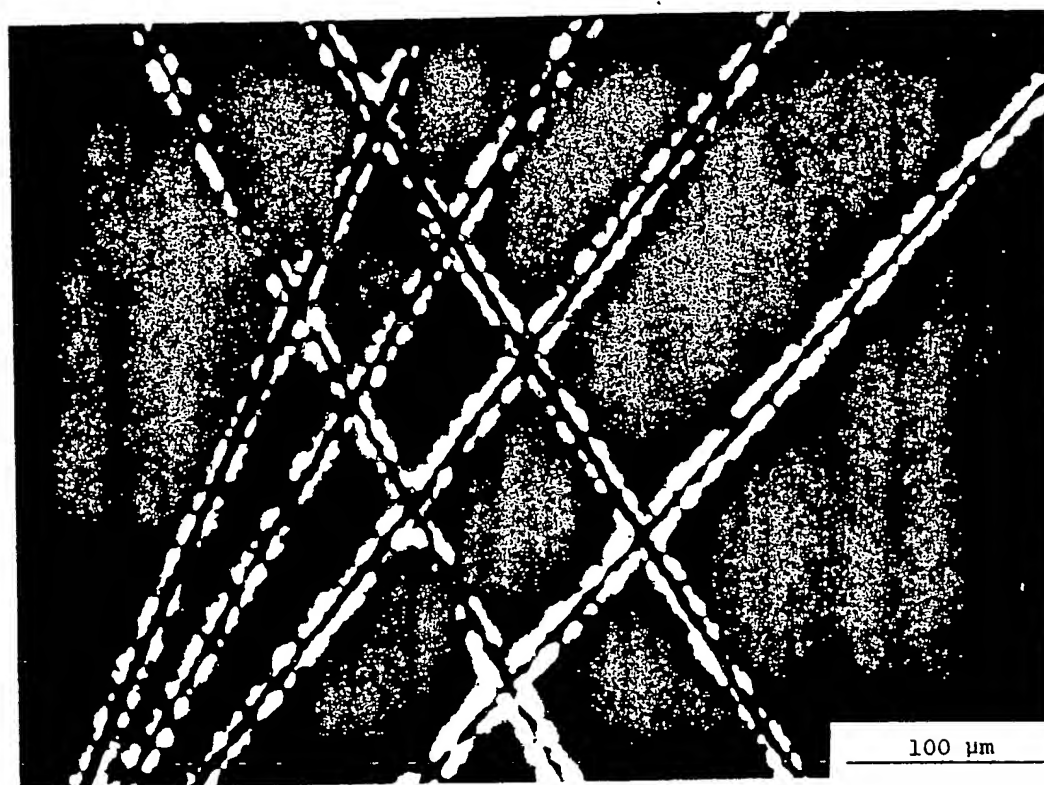


Fig. 8



SPECIFICATION

Carbon fibre-thermoplastic resin composite

5. This invention relates to a composite comprising highly crystalline carbon fibers and a crystalline thermoplastic resin epitaxially nucleated on the peripheral surface of the carbon fibers and then radially overcrystallized and to a method for the manufacture of the composite. The use of carbon fibers as a reinforcing material is popular in recent years and in most cases, thermosetting (cross-linking) resins represented by epoxy and alkyd resins are used as matrices.
- 10 To improve the adhesion between the two component materials, there is adopted a method of giving a proper chemical treatment to the surface of carbon fibers or a method of coating carbon fibers by the so-called coating or sizing process. In short, the object of such a surface treatment is to confer upon the surface of carbon fibers "chemical affinity" for the resin with which the fibers are desired to form a composite. It is generally accepted that the most difficult problem to
- 15 overcome in the production of a composite between carbon fibers and a thermoplastic resin is the tendency toward poor adhesion. Numerous attempts, including those mentioned above, have been made to improve the adhesion by surface treatments but none of these has been completely satisfactory.
- In the circumstances, there has been felt a strong need for perfection of a carbon fiber-thermoplastic resin composite wherein the surface of the carbon fibers and the resin serving as
- 20 the matrix are bound to each other so strongly that the composite as a whole enjoys good mechanical properties.
- The inventors presumed that it might be possible to realize such ideal composition by taking advantage of the "physical affinity" brought about by the epitaxy of some proper crystalline
- 25 polymer on the regular crystal surface of highly crystalline carbon fibers, and in pursuing this presumption through various studies, accomplished the present invention.
- It is common to control the nucleation of a polymer by addition of nucleating agents. However, practically few substances have been known to be capable of controlling the mode of the subsequent growth of the crystal and giving orientation to the crystallization as well as
- 30 promoting the nucleation of a polymer. The whisker-shaped polyoxymethylene needle-shaped single crystals developed by the inventors (U.S. Patent No. 4,026,873) are probably the only substance known to fulfil this requirement. It has been ascertained that this substance performs the aforementioned functions on several crystalline polymers (M. Iguchi and Y. Watanabe: "Polymer", 18, 265, 1977). Although it is only natural that the polyoxymethylene needle-
- 35 shaped single crystals have the effective mentioned on polyoxymethylene resin, which is chemically the same substance, it has now been found that the crystals are similarly effective on polyethylene and other polymers which have different crystal lattices from polyoxymethylene. This fact suggest the possibility of wider utilization of this technical idea.
- For successful induction of epitaxy of a molten resin on a separate substance added thereto,
- 40 two prerequisites are that the resin itself be crystalline in nature and that the substance thus added possess a crystalline surface.
- The present invention has been accomplished on the basis of the knowledge described above.
- One object of the present invention is to provide a composite which uses carbon fibers as a reinforcing material for a thermoplastic resin and which enjoys sound adhesion between them.
- 45 Another object of the present invention is to provide a method for the manufacture of a composite comprising carbon fibers and a thermoplastic resin which adhere soundly to each other.
- According to the present invention, there is provided a carbon fiber-thermoplastic resin composite, which comprises highly crystalline carbon fibers having undergone no surface
- 50 treatment, possessing a crystallite size of 50 Å or over in the direction of the [001] plane and possessing a regular crystal surface and a highly crystalline thermoplastic resin allowed to attain epitaxial nucleation radially on the peripheral surface of said carbon fibers and subsequent overgrowth crystallization in the cylindrical form, whereby the carbon fibers and the thermoplastic resin are bound at their interface by virtue of van der Waal's force.
- 55 The invention also provides a method for the manufacture of a carbon fiber-thermoplastic resin composite, which method comprises mixing highly crystalline carbon fibers having undergone no surface treatment, possessing a crystallite size of 50 Å or over in the direction of the [001] plane and possessing a regular crystal surface with a highly crystalline thermoplastic resin before the resin undergoes spontaneous nucleation at a still lower temperature for thereby
- 60 allowing the thermoplastic resin to attain epitaxial nucleation and subsequent overgrowth crystallization radially on the peripheral surface of carbon fibers, whereby the composite consequently produced will have the carbon fibers and the thermoplastic resin bound with each other by virtue of van der Waal's force exerted at their interface.
- consequently produced will have the carbon fibers and the thermoplastic resin bound with each
- 65 other by virtue of van der Waal's force exerted at their interface.

Figures 1, 2 and 3 represent a process for the formation of the composite of the present invention.

Figures 4, 5 and 6 represent a process for the formation of a composite different from that of the present invention wherein the carbon fibers are not effective for the epitaxy of thermoplastic resin and, therefore, the resin forms spherulitic crystals.

Figures 7 and 8 are photomicrographs taken at 300 magnifications of a process for the formation of the composite of the present invention as described in Example 3.

Highly crystalline carbon fibers for use in the composite of this invention will be described.

The origin of the carbon fibers is not critical. What is important is that the carbon fibers produced, should possess high crystallinity, namely that the crystal lattice on the surface of carbon fibers should possess high regularity. The crystallinity of carbon fibers is determined by their production process, particularly the degree of their carbonization; it increases with the temperature at which they are carbonized. In the present invention the crystallinity of carbon fibers as determined in terms of the crystallites' size in the direction of the [001] plane as determined by the X-ray diffraction should be at least 50 Å, preferably not less than 120 Å. A larger crystal naturally has a more highly regular crystal lattice on its surface and is, therefore, of greater crystallinity.

It is also essential that the carbon fibers not be given any surface treatment, i.e. the fibers should possess a neat surface. Therefore, those carbon fibers which have been treated for improving the adhesion to a thermosetting resin cannot be used for the present invention. Even if carbon fibers are not subjected to any such preparatory surface treatment, they prove unsuitable for the present invention when they are left to stand in the air so long after the carbonization as to cause a change in their surface condition.

Examples of highly crystalline thermoplastic resins which are useful for the present invention include polyacetal resins represented by polyoxymethylene-diacetate and copolyoxymethylene-oxyethylene resins; polyolefin resins represented by high-density polyethylene and polypropylene resins; polyamide resins; and polyester resins.

The production of the composite of this invention is accomplished by a procedure comprising the steps of first mixing the thermoplastic resin with the carbon fibers while the resin is held at a temperature capable of melting the resin and subsequently cooling the resultant mixture to the temperature of crystallization. During the first stage of this cooling, the resin undergoes epitaxial nucleation on the peripheral surface of the carbon fibers. If the cooling speed is too fast, an unwanted phenomenon of spontaneous nucleation tends to take place. It is, therefore, important that the cooling should be carried out under conditions controlled so that the epitaxial nucleation occurs preferentially. In the latter stage of the cooling, there proceeds a phenomenon of overgrowth crystallization, giving rise to a crystal possessing a unique radially oriented structure around the carbon fibers.

The term "epitaxy" refers to the oriented nucleation of a substance on the peripheral surface of a crystalline substrate and the term "overgrowth crystallization" to the growth of crystal which ensues from the epitaxial nucleation.

The composite of the present invention which is produced as described above has the carbon fibers and thermoplastic resin adhered strongly to each other by so-called "physical affinity". Although the two component substances are bound with each other by van der Waals force which is much weaker than the covalent bond, the contact between them is so perfect as to produce a strong adhesion as a whole. The adhesion due to this "physical affinity" differs in mechanism from the adhesion due to the "chemical affinity" produced between the pretreated surface of a carbon fiber and a thermosetting resin.

Now, the present invention will be described in further detail.

As is well known a crystalline polymeric substance in a molten state solidifies at a suitable supercooling temperature below its melting point. The process of this solidification, as well as the crystallization process of other substance, comprises two discrete steps, namely nucleation and growth. Thermodynamically, nucleation is much more difficult to attain than growth. It is frequently experienced that even under supercooling conditions of ample potentiality of growth, solidification does not occur due to the lack of nuclei. It is also well known that the presence of a different substance accelerates nucleation. Therefore, the practice of adding granules called nucleating agent to the polymers in their molten state is generally adopted. In the present invention, it is the one-dimensional shape possessed by the regular crystal surface of the highly crystalline carbon fibers that plays the part of such a nucleating agent. To be more specific, when carbon fibers of the foregoing description are placed in the molten polymer and the resultant mixture is cooled, chain-molecules of the molten polymer deposit along the crystal lattices throughout the entire surface of the carbon fibers and the deposited molecules function as nuclei which promote the subsequent growth of crystals. Owing to the epitaxy and subsequent overgrowth crystallization of the thermoplastic resin caused as described above, the resin will form crystallites cylindrically oriented around the carbon fibers.

The epitaxy of the resin on the surface of each carbon fiber occurs in preference to the so-

called "sporadic nucleation" which can be induced without resorting to any special measure, no matter whether the crystallization is carried out at a constant temperature of crystallization or it is carried out under a continuously cooled condition. Generally when the carbon fiber content in the composite falls in the range of from 1.0 to 50% by weight, therefore, the composite finally produced will as a whole be constitute of an aggregate of cylindrical structures and will not include spherulitic crystals which would result from ordinary nucleation.

Formation of a composite by use of carbon fibers having high crystallinity and the function of surface epitaxy and that by use of carbon fibers not having an epitaxially functioning surface are compared in terms of steps of crystal growth in Figs. 1, 2 and 3 and Figs. 4, 5 and 6. In the drawings, numeral 1 denotes a carbon fiber, 2 a cylindrical crystal of thermoplastic resin formed radially on the peripheral surface of the carbon fiber and 3 a spherulitic crystal of thermoplastic resin. Figs. 2 and 3 illustrate gradual growth of cylindrical crystals. Eventually all the thermoplastic resin is used up in the growth of these cylindrical crystals around the carbon fibers. In contrast the carbon fibers shown in Figs. 4, 5 and 6 are destitute of epitaxial function, so that the thermoplastic resin attains growth in the form of spherical crystals in the intervening spaces between the carbon fibers.

The cooling to which the mixture of carbon fibers with the thermoplastic resin in its molten state is subjected for the purpose of inducing epitaxial nucleation and subsequent overgrowth crystallization will now be described.

In the first stage of the cooling, surface nucleation takes place. As the cooling is further continued, an unwanted phenomenon of free nucleation tends to follow. To preclude spontaneous nucleation as much as possible and to ensure preferential occurrence of epitaxial nucleation and overgrowth crystallization on the surface of carbon fibers, it is highly undesirable for the mixture to be cooled fast to very low temperatures. The speed at which this cooling should be carried out is variable with the crystallinity of the carbon fibers in use, the amount of carbon fibers used in the composite and the kind of thermoplastic resin in use and, therefore, cannot be fixed by a general rule. When the cooling is effected at the temperature of crystallization, however, there can be applied a common procedure that the mixture may be maintained at a constant temperature of crystallization or it may be cooled gradually at a temperature decrease rate of not more than 20°C/min.

In the case of a polyoxymethylene resin, for instance, it is necessary to select conditions such that the crystallization is completed at temperatures in the range of from 150 to 155°C. In the case of a polyethylene resin, the conditions to be selected must be such that the crystallization is completed at temperatures of not less than 115°C.

It should be noted that a phenomenon of heterogeneous nucleation will possibly ensue when the temperature of melting is not high enough or when the resin is subjected to a shearing force in the course of cooling.

In the production of the composite of this invention in a prescribed shape, the shaping of the molten mixture should be carried out at temperatures of not less than 190°C in the case of a polyoxymethylene resin or not less than 170°C in the case of a polyethylene resin, with special care taken not to expose the shaped mixture to any shearing force.

The composite of this invention may incorporate therein a stabilizer, an antioxidant and other commonly used additives. It is nevertheless undesirable for the composite to incorporate therein a nucleating agent as is commonly used.

The composite produced as described above possesses properties considerably different from those which are exhibited by the ordinary composite in which the resin has not produced any epitaxial nucleation on the surface of carbon fibers. Specifically, the composite enjoys outstanding adhesion between the resin and carbon fibers and, consequently, exhibits superior mechanical properties.

In the case of a composite which is made up of carbon fibers having been subjected to a surface treatment and a thermoplastic resin, for example, the carbon fibers do not induce any nucleation of the resin on the their surface and consequently have no sound adhesion to the resin. When this composite is fractured, separation of the resin from the surface of carbon fibers is clearly observed in the surface of fracture. In sharp contrast, in the case of the composite of the present invention, the carbon fibers and the resin are so strongly adhered to each other that when it is fractured, the fracture will be formed evenly across the texture of the composite without producing any separation in the interface between the two component substances.

Since the composite of the present invention possesses such outstanding properties as compared with the conventional carbon fiber-thermoplastic resin composite, it brings about an excellent effect when it is used as a material which must undergo repeated application of stress such as, for example, materials for leaf springs, screws and gear wheels.

Now the present invention will be described in further detail with reference to working examples.

Example 1:

In 95 parts by weight of a high-density polyethylene having a viscosity-averaged molecular weight of 5.2×10^4 and melted by heating to 175°C , there were placed 5 parts by weight of highly crystalline carbon fibers having been subjected to no surface treatment (possessing a crystallite size of 180 \AA in the direction of [001] plane). The carbon fibers were arranged in a parallel bundle. The bundle immersed in the resin was placed between two glass plates and was allowed to cool to normal room temperature at a temperature decrease rate of about $20^\circ\text{C}/\text{min.}$, to produce a plate-shaped composite.

In the course of the cooling, the resin was observed through a polarized microscope to determine its state of crystallization. In the neighborhood of 120°C , epitaxy and overgrowth of the resin were clearly observed on the entire surface of the carbon fibers. Thereafter cylindrical crystals of the resin were observed to gain gradually in growth.

Referential Example 1-1:

The procedure of Example 1 was followed, except there were used carbon fibers of untreated surface and low crystallinity (having a crystallite size of 24 \AA in the direction of the [001] plane). In the course of the cooling, the microscopic observation was performed similarly. Although nucleation and crystal growth were observed in the neighborhood of 120°C , the density of points of nucleation was low as compared with that obtained in Example 1.

Referential Example 1-2:

The procedure of Example 1 was followed, except there were used highly crystalline carbon fibers having undergone a surface treatment. In the microscopic observation similarly performed in the course of cooling, neither nucleation nor crystal growth was observed at all on the surface of carbon fibers. In the neighborhood of 115°C , growth of spherical crystals was observed.

Example 2:

In 90 parts by weight of a polyoxymethylene diacetate having a viscosity-averaged molecular weight of 1.57×10^4 and melted by heating at 195°C , there were placed 10 parts by weight of highly crystalline carbon fibers having undergone no surface treatment (possessing a crystallite size of 180 \AA in the direction of the [001] plane). The carbon fibers were arranged in a parallel bundle. The bundle immersed in the resin was interposed between two glass plates and was allowed to cool to normal room temperature at a temperature decrease rate of about $20^\circ\text{C}/\text{min.}$ to produce a plate-shaped composite 5 mm in thickness.

In the course of this cooling, the composite was kept under observation through a polarized microscope. In the neighborhood of 160°C , epitaxy of the resin was observed to occur on the entire surface of fibers and formation of cylindrical crystals was observed to ensue.

Referential Example 2-1:

The procedure of Example 2 was followed, except there were used carbon fibers of low density having undergone no surface treatment (possessing a crystallite size of 24 \AA in the direction of the [001] plane). In the microscopic observation similarly performed in the course of cooling, there was observed very slight coarse nucleation on the surface of the carbon fibers.

Referential Example 2-2:

The procedure of Example 2 was followed, except there were used the same carbon fibers having undergone a surface treatment as in Referential Example 1-2. In the microscopic observation similarly performed, neither nucleation nor crystal growth was observed at all on the surface of carbon fibers. In the neighborhood of 150°C , formation of spherical crystals was observed.

The composites obtained in Example 2 and Referential Example 2-2 were fractured parallelly with the direction in which the carbon fibers were arranged in the bundle and their surfaces of fracture were observed. It was consequently ascertained that, in the composite of Example 2, the fracture occurred across the portion of resin and did not affect the interface between the resin and carbon fibers and, in the composite of Referential Example 2-2, the fracture occurred in the form of separation along the interface between the resin and the carbon fibers.

Example 3:

At 190°C , 95 parts by weight of an isotactic polypropylene having a viscosity-averaged molecular weight of 1×10^5 and 5 parts by weight of highly crystalline carbon fibers having undergone no surface treatment (possessing a crystallite size of 180 \AA in the direction of the [001] plane) were mixed. The resultant mixture was cooled in the same manner as in Example 1, to afford a plate-shaped composite 5 mm in thickness.

In the observation performed of the composite while in cooling through a polarized microscope, it was ascertained that epitaxy of the resin started forming radially on the entire

periphery of the carbon fibers in the neighborhood of 120°C and overgrowth crystallization in the cylindrical form ensued. Fig. 7 and Fig. 8 are photomicrographs taken at 300 magnifications of different stages of the formation of cylindrical crystals. Fig. 8 shows advanced degrees of crystal growth compared with the crystals shown in Fig. 7. No spherical crystals are found in these photographs.

Referential Example 3:

The procedure of Example 3 was followed, except there were used carbon fibers of low crystallinity having undergone no surface treatment (possessing a crystallite size of 24 Å in the direction of the [001] plane), to afford a composite. In the composite, epitaxy of the resin occurred very sparsely.

Example 4 and Referential Example 4:

By following the procedure of Example 1, composites having a polyoxymethylene diacetate resin as their matrices were produced using highly crystalline carbon fibers having undergone no surface treatment (possessing a crystallite size of 180 Å in the direction of the [001] plane) and similar carbon fibers coated with an epoxy resin. The composites were compared in terms of mechanical properties. Both carbon fibers having an average length of 5 mm were packed as uniformly as possible in the molten resin and compressed with a hot press to produce plate-shaped test pieces about 0.2 mm in thickness. In this case, the fibers were arranged substantially in a planary orientation.

The mechanical properties were determined with an Instron tester under standard temperature and humidity conditions, with the sample length fixed at 5 cm (0.5 cm in width) and the tensile rate of 2 mm/min.

The results are shown in the following table.

Item	Carbon fibers	Carbon fiber content (%) in composite			
		2.5	5	7.5	10
Strength kg/cm ²	A	516	577	577	546
	B	482	481	530	403
Elongation (%)	A	7.3	6.4	6.5	3.0
	B	5.2	4.6	4.9	2.5

A: Carbon fibers without any surface treatment

B: Carbon fibers coated with epoxy resin

It is seen from the table that in all the composites having varying carbon fiber contents, the carbon fibers (A) having undergone no surface treatment showed improvement of strength of from 10 to 30% and considerable improvement of elongation compared with the carbon fibers (B) coated with the epoxy resin. These better results are ascribable to improvement in interfacial adhesion resulting from the epitaxy and overgrowth crystallization obtained on the peripheral surface of these carbon fibers (A).

CLAIMS

1. A carbon fiber-thermoplastic resin composite, which comprises highly crystalline carbon fibers having undergone no surface treatment, possessing a crystallite size of 50 Å or over in the direction of the [001] plane and possessing a regular crystal surface and a highly crystalline thermoplastic resin allowed to attain epitaxial nucleation radially on the peripheral surface of said carbon fibers and subsequent overgrowth crystallization in the cylindrical form, whereby the carbon fibers and the thermoplastic resin are bound at their interface by virtue of van der Waals force.
2. The composite according to claim 1, wherein the thermoplastic resin is one member selected from the group consisting of polyacetal resins, polyolefin resins, polyamide resins and polyester resins.
3. The composite according to claim 1, wherein the carbon fibers have a size of 120 Å or over in the direction of the [001] plane.
4. The composite according to claim 1, wherein the carbon fiber content of the composite is in the range of from 1.0 to 50% by weight.

5. A method for the manufacture of a carbon fiber-thermoplastic resin composite, which method comprises mixing highly crystalline carbon fibers having undergone no surface treatment, possessing a crystallite size of 50 Å or over in the direction of the [001] plane and possessing a regular crystal surface with a highly crystalline thermoplastic resin at a temperature
- 5 capable of melting only the thermoplastic resin and subsequently cooling the resultant mixture to a temperature capable of inducing solidification (crystallization) of the resin before the resin undergoes spontaneous nucleation at a still lower temperature for thereby allowing the thermoplastic resin to attain epitaxial nucleation and subsequent overgrowth crystallization
- 10 radially on the peripheral surface of carbon fibers, whereby the composite consequently produced will have the carbon fibers and the thermoplastic resin bound with each other by virtue of van der Waals force exerted at their interface. 10
6. The method according to claim 5, wherein the thermoplastic resin is one member selected from the group consisting of polyacetal resins, polyolefin resins, polyamide resins and polyester resins.
- 15 7. The method according to claim 5, wherein the carbon fibers have a crystallite size of 120 Å or over in the direction of the [001] plane. 15
8. The method according to claim 5, wherein the carbon fiber content of the composite is in the range of from 1.0 to 50% by weight.
9. A method as claimed in claim 5 and substantially as herein described in any one of the
- 20 specific examples hereinbefore set forth. 20